AD-A120 341 EVANS (CHARLES) AND ASSOCIATES SAN MATEO CA F/G 20/7
A DOD/DESAT PHASE I FINAL REPORT.(U)
JUN 82 C A EVANS, C J HITZMAN N00014-82-C-0141
UNCLASSIFIED NL

1 of 1
AD A
120341

END
DATE
FILMED
11-82
DTIC

(12)

CHARLES EVANS & ASSOCIATES

SPECIALISTS IN MATERIALS CHARACTERIZATION

AD A120341

A DoD/DESAT PHASE I FINAL REPORT

Project Title THE USE OF SURFACE ANALYTICAL TECHNIQUES TO ELUCIDATE SEMICONDUCTOR CRYSTAL GROWTH.

Submitted by Charles Evans & Associates
San Mateo, California

Submitted to Office of Naval Research
Department of the Navy
Arlington, Virginia

Submission Date June 30, 1982

Report Prepared by Dr. Charles A. Evans, Jr.
and Mr. Charles J. Hitzman

N00014-82-C-0141

82 10 14 038

1670 SOUTH AMPHLETT BOULEVARD • SUITE 120 • SAN MATEO, CALIFORNIA 94402
(415) 572-1601 • Telex 172747

TABLE OF CONTENTS

I. PROJECT SUMMARY

The purpose of this Phase I research program was to determine the ability of combining carefully planned crystal growth experiments with surface sensitive spectroscopies to elucidate fundamental phenomena in semiconductor crystal growth methods. This study has employed high performance secondary ion mass spectrometry (SIMS) and other surface sensitive spectroscopies such as scanning electron microscopy (SEM), Auger electron spectroscopy (AES), and energy dispersive X-ray spectrometry (EDS) in the study of thin crystalline films grown by organometalic vapor phase epitaxy (OMVPE), molecular beam epitaxy (MBE), and liquid phase epitaxy (LPE) processes. The ultimate goal of this research is to provide insight into the mechanisms involved in these crystal growth methods. Studies have also employed a new rapid isothermal annealing system for the solid phase crystal regrowth of ion implanted silicon.

The results of several of the Phase I activities have been submitted for journal publication and for presentation at appropriate conferences. The following papers have been accepted for presentation at and publication in the proceedings of the International Symposium on GaAs and Related Compounds to be held September 19-22, 1982 in Albuquerque, New Mexico:

1) Spatially Correlated Redistribution of Mn and Ge in In_{1-x} Ga_x As MBE layers, E. Silberg, T.Y. Chang, and E.A. Caridi, Bell Laboratories, Holmdel, NJ 07733

and

C. A. Evans, Jr. and C. J. Hitzman, Charles Evans & Associates, San Mateo, CA 94402

2) Growth of Planar Doped Barrier Structures in Gallium Arsenide by Molecular Beam Epitaxy, S.C. Palmateer, P.A. Moki, M.A. Hollis, L.F. Eastman, School of Electrical Engineering, Cornell University, Ithaca, NY 14853

and

Ian D. Ward, Charles Evans & Associates, San Mateo, CA 94402

3) Si Incorporation in Al_xGa_{1-x} As Grown by Molecular Beam Epitaxy T.J. Drummond, W.G. Lyons, R. Fisher, R.E. Thorne, and H. Morkoc, Department of Electrical Engineering, Coordinated Science Laboratory, University of Illinois, Urbana, IL 61801

and

C.G. Hopkins and C.A. Evans, Jr., Charles Evans & Associates, San Mateo, CA 94402

The last of these has been submitted to <u>The Journal of Vacuum Science and Technology</u>, and will not appear in the conference proceedings.

II. CONCEPTS AND APPROACH

In recent years, great advances have been made in the development of smaller, faster and more sophisticated semiconductor devices. These advances have placed tremendous demands on the materials used for the fabrication of these devices. The need for high purity, single crystal thin films with carefully controlled thickness and doping levels demands a detailed physical understanding of the crystal growth process.

A variety of surface analytical techniques have been developed to meet the assessment requirements of semiconductor science and technology. We have combined our expertise in the use of these surface sensitive spectroscopies for materials characterization with the insights and knowledge provided by consultants and collaborators in the field of advanced crystal growth to better understand both the pertinent growth processes and the materials produced by these emerging technologies.

III. RESULTS AND DISCUSSION

A. Introduction

In the research proposal we stated our goal to be:

> "In Phase I we plan to evaluate the ability of high performance secondary ion mass spectrometry (SIMS) and organometalic vapor phase epitaxy (OMVPE) deposition of III/V compounds and alloys to provide

insight into the atomic mechanism involved in this crystal growth method. If the SIMS analysis of these materials is sufficiently informative, we would expand the analysis using other surface sensitive spectroscopies (i.e. scanning Auger microscopy and Rutherford backscattering(RBS) in order to completely characterize these materials during Phase II. The utilization of all of these techniques would permit a detailed examination of OMVPE grown films, and would allow for expansion of the research into other existing and emerging crystal growth technologies."

Not only did we accomplish the above stated goal of evaluating the use of surface sensitive spectroscopies but feel we actually progressed beyond this goal to the initial evaluation of other crystal grwoth methods (MBE and LPE) using the SIMS and combined SEM/AES/EDS techniques. Because of the importance of these evaluations in elucidating the real issues in the study of thin film crystal growth methods, several manuscripts have been prepared and accepted for presentation and publication in the proceedings of the 1982 International Symposium on GaAs and Other Related Compounds.

The following discussion summarizes the significant results obtained in this Phase I research effort.

B. Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy is a crystal growth technique which evolved from vacuum evaporation technology. It is a powerful technique in that it makes possible the layer by atomic layer growth of semiconductor compounds and alloys.

Many III/V compounds and their ternary and quaternary alloys have been produced using MBE methods.

The SIMS technique is ideally suited to the analysis of films grown by MBE because, in essence, SIMS performs a "layer by atomic layer" removal and trace element analysis of these thin films. During the course of this Phase I research, we have performed the following studies using SIMS to analyze films grown by MBE:

1) SI Incorporation in $Al_xGa_{1-x}As$ Grown by MBE in conjunction with Professor H. Morkoc of the Department of Electrical Engineering and Coordinated Science Laboratory at the University of Illinois, Urbana-Champaign.

2) Spatially correlated redistribution of Mn and Ge in InGaAs MBE layers in conjunction with E. Silberg, T.Y. Chang and E.A. Caridi at Bell Laboratories in Holmdel, New Jersey.

3) Growth of planar doped structures in GaAs by MBE in conjunction with Professor C. Wood and Professor L. Eastman of the School of Electrical Engineering at Cornell University.

A discussion of each of these studies follows:

1) The $Al_xGa_{1-x}As$ alloy system has been the subject of extended research because of its importance in opto-electric devices. The incorporation of the n-dopant Si in $Al_xGa_{1-x}As$ layers grown by MBE was studied as a function of

substrate growth temperature and Si cell temperature (Si arrival rate at the substrate). The correlation between the atomic concentrations in this system (determined by SIMS analysis) and net electron concentrations (determined by the Van der Pauw-Hall technique) supported three important conclusions:

a) The deposited Si sticking coefficient decreases with increasing substrate growth temperature.

b) All of the Si incorporated is electrically active and n-type up to about 4×10^{18} cm^{-3} above which Si precipitation is observed.

c) No sign of Si depletion or accumulation at either the surface or the interface was detected throughout the growth temperature range investigated.

Figure 1 shows the Si atomic and net electron concentration as a function of growth temperature. The SIMS and Hall data are in good agreement indicating that all the Si atoms are incorporated into the group III sublattice. The decrease in Si concentration with increasing growth temperature (above 650°C) indicates re-evaporation of Si from the growing film.

The Si atomic and net electron concentration as a function of Si cell temperature is shown in Figure 2. The agreement between SIMS and Hall data supports the conclusion that all of the Si incorporated is electrically active (100% doping efficiency). When the Si cell temperature is increased above 1150°C the electron concentration remains constant but the atomic concentration increases.

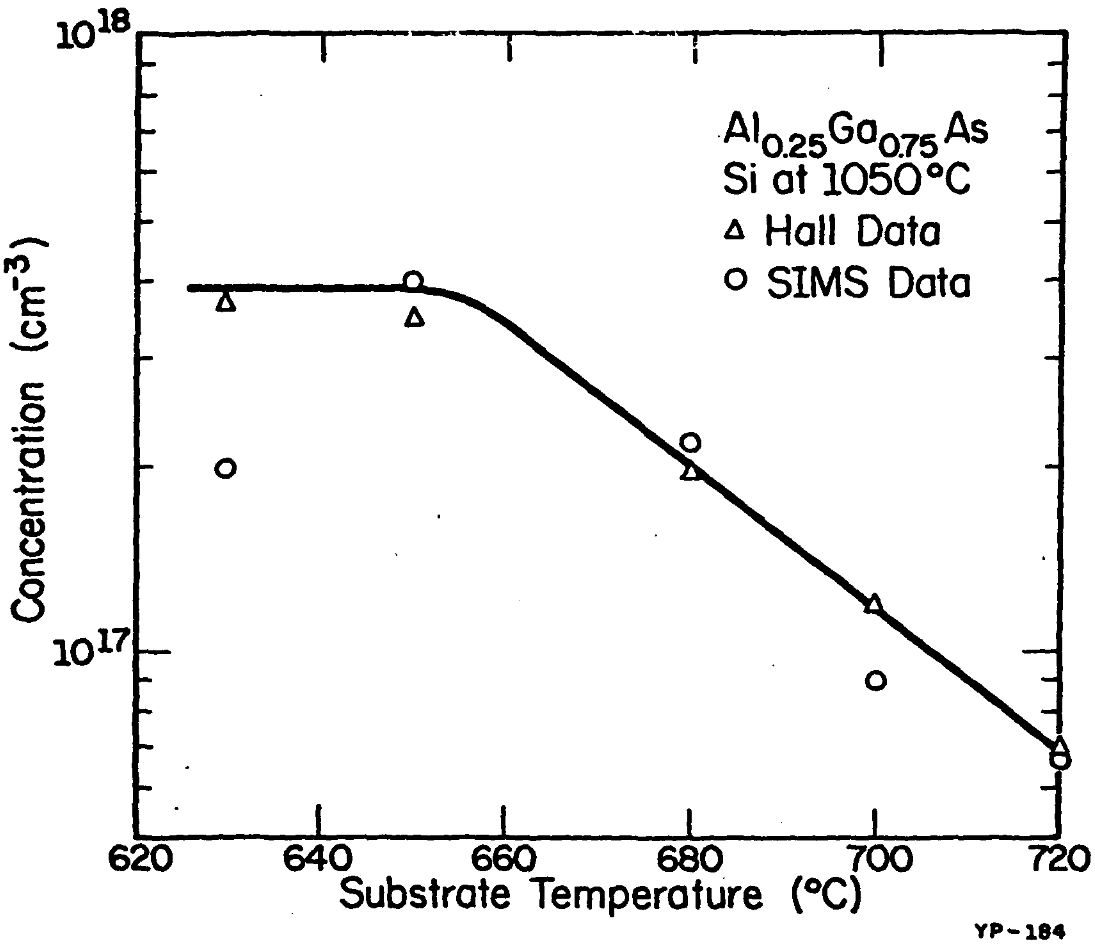


FIGURE 1- Si atomic concentration (SIMS data) and net electron concentration (Hall data) as a function of substrate growth temperature.

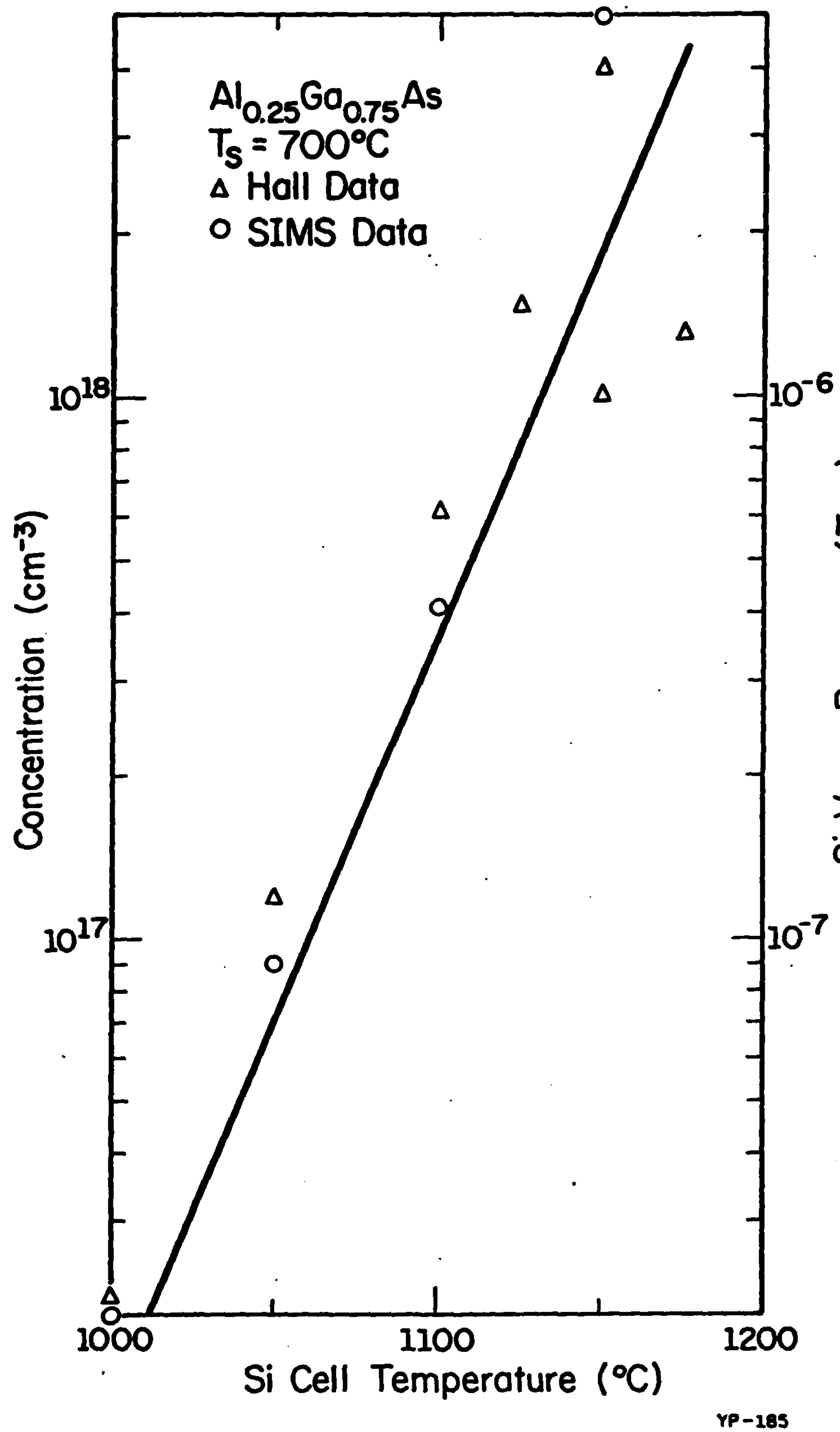


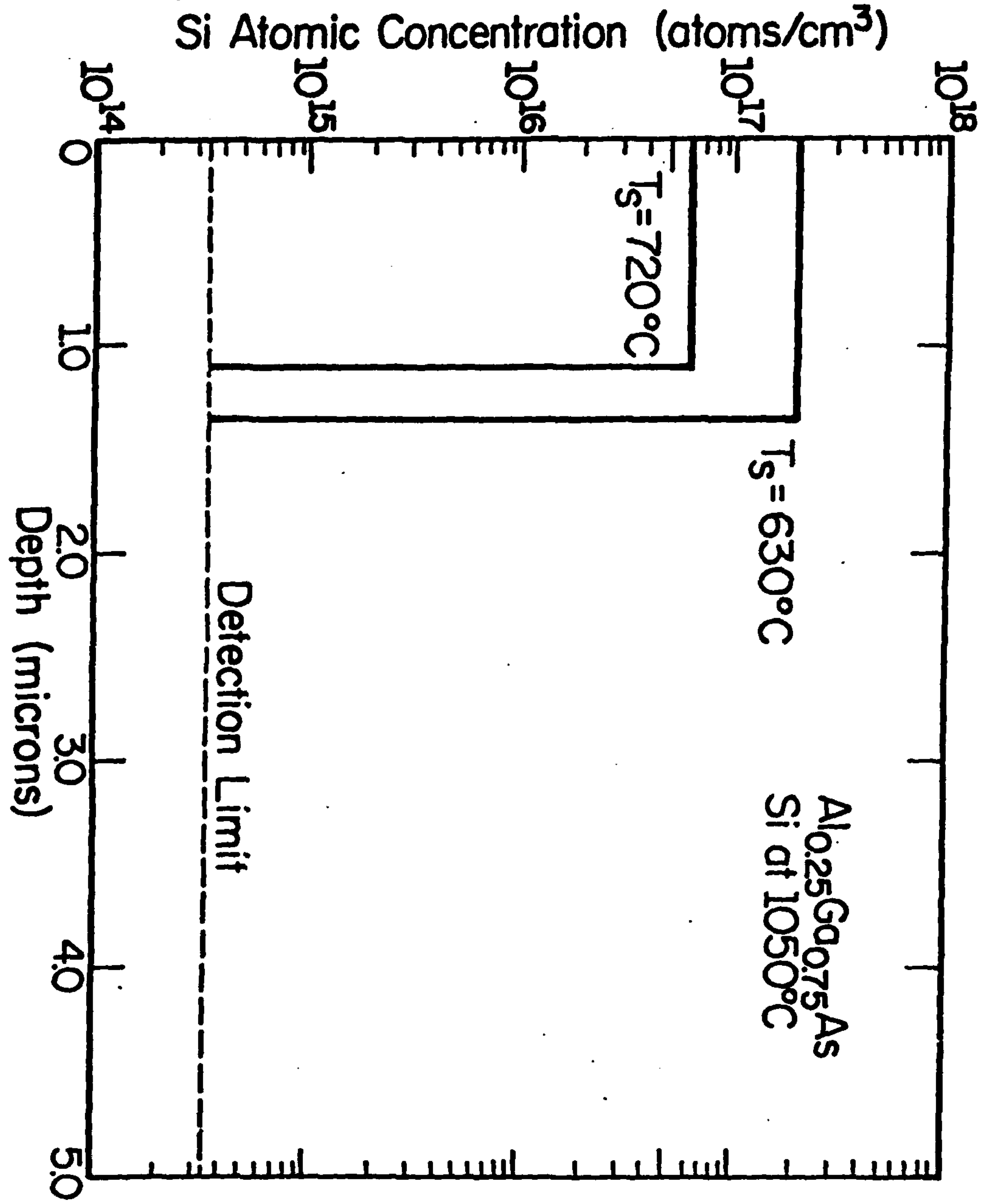
FIGURE 2- Si atomic concentration and net electron concentration as a function of Si cell temperature.

This observation implies the onset of Si precipitation which was subsequently confirmed using a selective etch and optical microscopy.

Figure 3 shows SIMS depth profiles for Si incorporated at growth temperatures of 630°C and 720°C. The profiles indicate no accumulation or depletion of Si at the outermost surface or at any interface. The attainment of such sharp doping profiles is critical to final device performance. Thus the sensitive depth profiling capabilities of SIMS along with the interpretation of correlations between SIMS and electrical data have provided a better understanding of Si incorporation in AlGaAs MBE layers.

2) A group headed by Drs. T. Chang and E. Silberg of Bell Laboratories in Holmdel, New Jersey, have been involved in growing Mn and Ge doped InGaAs MF layers on InP for applications to lasers and optical communications systems. In the course of our normal commercial analytical work for this group, we observed a phenomenon that had been predicted but never conclusively demonstrated experimentally viz. a colligative interaction between impurities in a semiconductor material. We discussed this effect with Drs. Chang and Silberg and they agreed to prepare samples for a collaborative study conducted under the auspices of this Phase I research program. Although the preparation of these samples was not directly related to their main research activity, these samples would possibly demonstrate the dependence of Mn redistribution or its diffusion coefficient on local Ge concentrations in the InGaAs MBE layers. Experiments were carefully designed and performed in an attempt to accurately test the possible association between the two dopants.

Films were grown by MBE with Mn doping pulses alone as well as Mn doping pulses



YP-187

FIGURE 3- SIMS profiles of Si atomic concentration for substrate growth temperatures 630°C and 720°C.

in the presence of a Ge doping background. The films were then annealed under a variety of conditions, and two series of as-grown and annealed films analyzed by SIMS to obtain depth profile distributions of the Mn and Ge dopants. Figure 4 shows the theoretical Mn doping and the actual Mn profiles for the as-grown epilayers as well as after 4 hours of annealing at 650°C and 700°C in the absence of intentional Ge doping. Figure 5 presents the Mn profiles for the films with a Ge doping background of approximately 1×10^{17} at-cm^{-3}. As can be readily seen, the diffusion coefficient for Mn drops about two orders of magnitude in the presence of Ge. This result indicates that there is an interaction of some sort between the Mn and Ge dopants. At this time, it is not clear whether this association is an atom-to-atom complexing or an effect resulting from a Fermi level shift. We believe that with careful design of future experiments the exact mechanism can be determined.

Not only does this particular study convincingly reveal an important solid state effect, it again illustrates the power of carefully planned crystal growth and characterization experiments. Furthermore, it supports another basic contention stated in our proposal that our commercial analytical activities and understanding of electronic materials provides a unique "window on the world" which permits us to observe and correlate the results of many unrelated materials research activities. With this broad overview, we are in a position to identify key issues which might otherwise be overlooked by a single, isolated research group.

3) Rectifying diodes based on planar doped barrier structures (n-i-p$^+$-i-n) have been fabricated by MBE using modulated doping in GaAs. The groups of Professors Wood and Eastman at Cornell University have been investigating the

PROCESSED DATA

CHARLES EVANS & ASSOCIATES 11-JUN-82 DEPTH PROFILE

20528

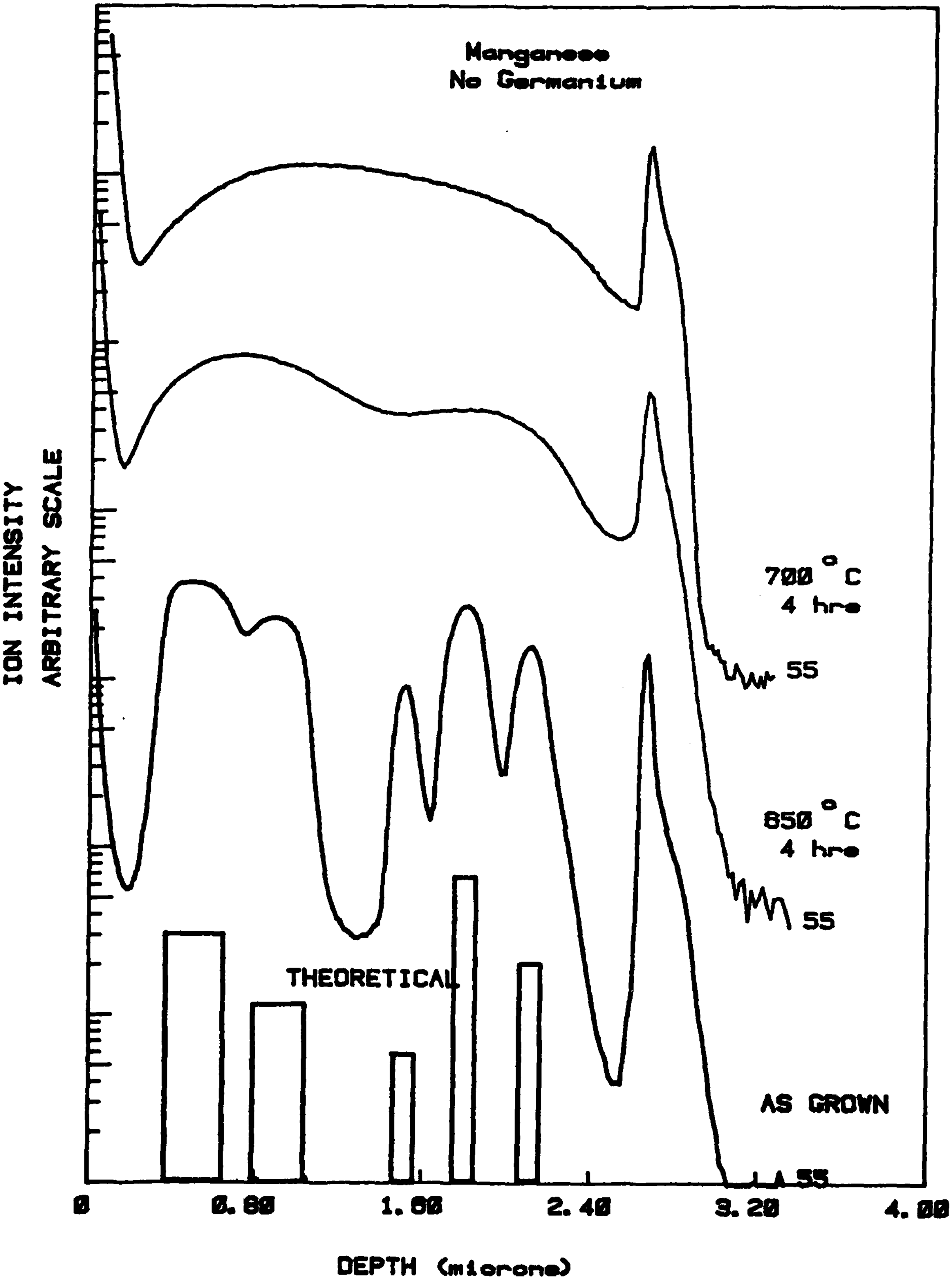


FIGURE 4

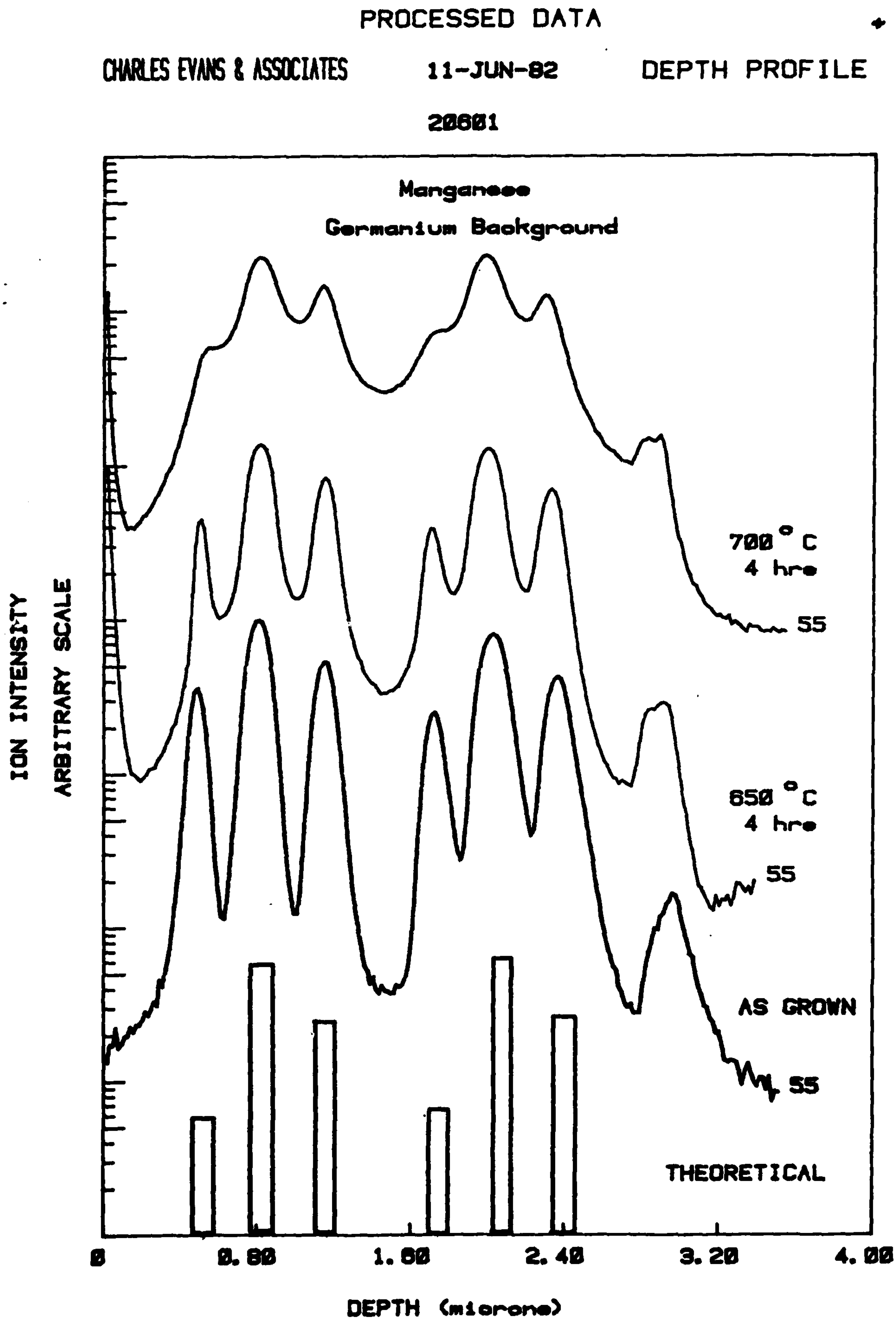

PROCESSED DATA
CHARLES EVANS & ASSOCIATES
11-JUN-82
DEPTH PROFILE
20601
Manganese
Germanium Background
ION INTENSITY
ARBITRARY SCALE
700 °C
4 hrs
55
650 °C
4 hrs
55
AS GROWN
55
THEORETICAL
0
0.80
1.60
2.40
3.20
4.00
DEPTH (microns)

FIGURE 5

conditions which affect the reproducibility and uniformity of these barrier structures grown by MBE methods. Structures were grown on silicon doped, tin doped, chromium doped and undoped GaAs substrates. Analysis of these various structures by SIMS depth profiling, showed an asymmetric spreading of the p^+ plane when growth occurred on Si doped substrates. The asymmetric spreading was not seen in the structures grown on the Sn doped, Cr doped or undoped substrates. Structures grown on Cr doped heat treated (the treatment prior to MBE growth) substrates results in precise control and 100% wafer uniformity of designed barrier heights.

Also in this study we observed unintentional Cr and Mn doping of the MBE layers grown on Cr doped GaAs substrates. Our SIMS analysis demonstrated that Mn and Cr segregated to the outermost surface of the growing layers during MBE deposition resulting in unintentional doping of the layer. The SIMS data further shows that this effect is eliminated when the layers are grown on substrates which were heat treated (750°C for 2 hours) and etched prior to crystal film growth.

C. Rapid Isothermal Annealing for Solid Phase Regrowth of Ion Implanted Silicon

In recent years, laser and electron beams have been used as heat sources for improved annealing of semiconductor wafers during processing. Along these lines a new CW lamp annealing process, HEATPULSE™, was developed and patented by AG Associates. HEATPULSE™ employs a microprocessor controlled system consisting of high intensity, tungsten-halogen lamps to rapidly heat a Si wafer to temperatures as high as 1250°C. This allows wafer wide ion implant activation

in times as short as 5-100 seconds. Charles Evans & Associates has purchased and installed a HEATPULSE^{TM} in our laboratory and we have begun studies on the use of the HEATPULSE^{TM} for solid phase regrowth of ion implanted silicon.

A significant advantage of HEATPULSE^{TM} annealing is that complete activation of the implanted species can be obtained without significant dopant or impurity diffusion. Figure 6 shows the SIMS depth profiles of an As^+ implant into polycrystalline Si after various HEATPULSE^{TM} treatments. The profiles show no observable dopant diffusion for annealing times of 15 seconds or less at various power levels. In addition, the sheet resistivities of the processed substrate material were found to lie between 78 kΩ cm^{-2} and 98 kΩ cm^{-2}. The sample which had been exposed to high temperatures for 60 seconds exhibited a diffusion length of about 300 Å and sheet resistivity increased to 171 kΩ cm^{-2} probably due to the inactivity of As atoms which diffused to poly Si grain boundaries during the annealing cycle.

Another important result of the transient nature of HEATPULSE^{TM} annealing is the absence of oxygen redistribution. Oxygen is intentionally incorporated into Cz-Si during growth for the following reasons:

1) wafer warpage problems are reduced

2) the mechanical strength of the wafer is increased

and 3) bulk SiO_x precipitates can be created to trap heavy metal impurities.

CHARLES EVANS & ASSOCIATES DEPTH PROFILE

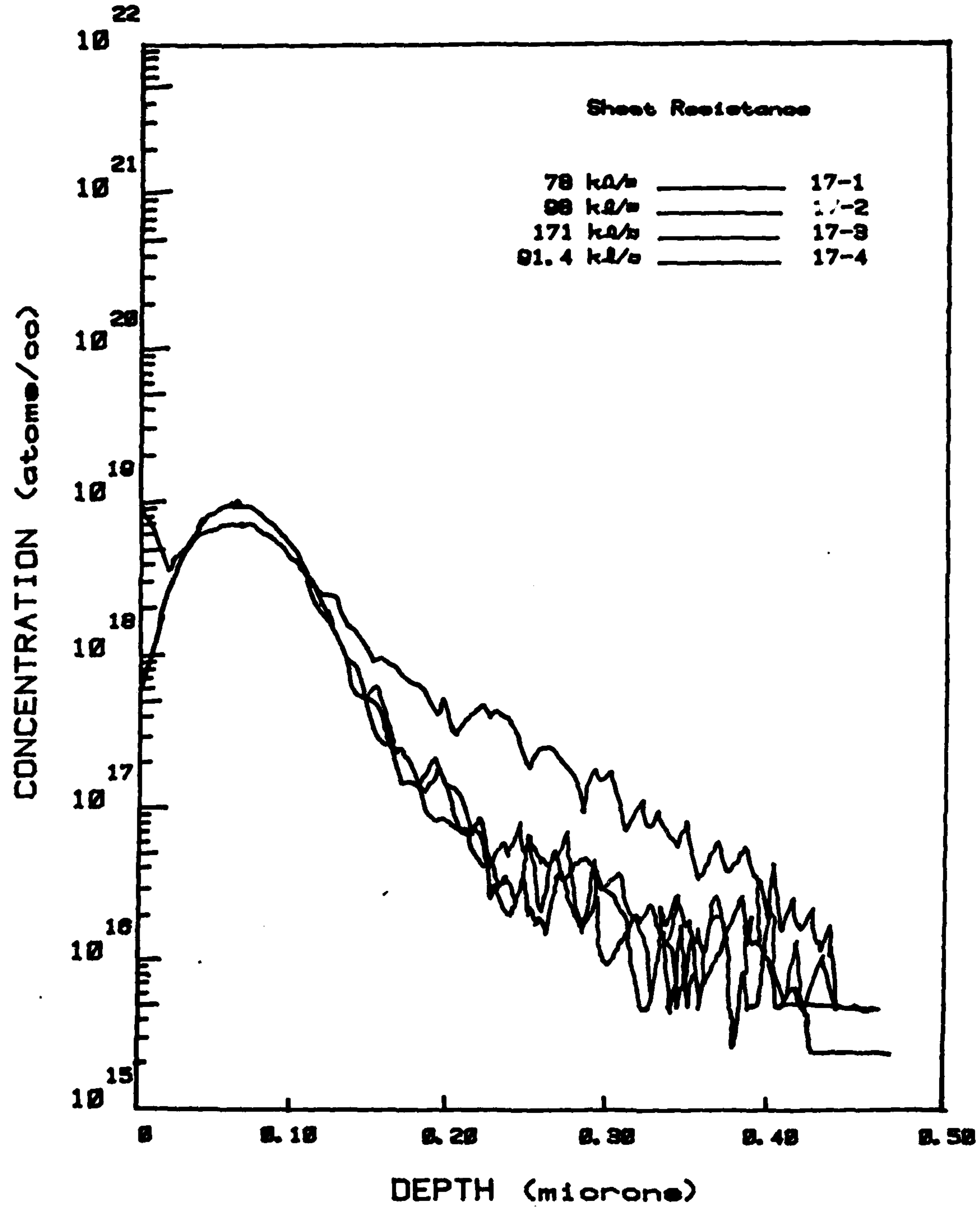


FIGURE 6- SIMS measurements on As concentration in polysilicon after various HEATPULSE™ treatments.

17-1 68% 15 sec 17-2 86% 15 sec
17-3 86% 60 sec 17-4 50% 60 sec

It has been observed, however, that interstitial oxygen can rapidly redistribute and "getter" into localized residual ion implant damage during conventional furnace annealing. This can prove to be deleterious in wafer processing and is probably the mechanism which causes emitter-collector shorts in bipolar transitors. Figure 7 shows SIMS depth profiles for oxygen in an As implanted Si wafer after HEATPULSE™ and conventional furnace annealing. No gettered oxygen is observed after the HEATPULSE™ anneal, which is in marked contrast to experimentally observed precipitation of oxygen near Rp for a similar ion implanted wafer using conventional furnace annealing. The control of oxygen diffusion in silicon wafers by HEATPULSE™ thermal processing is potentially one of the keys to the successful future of VLSI device fabrication. The coupling of HEATPULSE™ processing of VLSI devices with the trace level detection capabilities of the CAMECA IMS-3f Ion Microanalyzer in depth profile analysis of oxygen may provide the methodology for reproducible and reliable fabrication of these devices.

D) Organometallic Vapor Phase Epitaxy (OMVPE)

Organometallic vapor phase epitaxy is a chemical deposition technique for the formation of thin ($< 10\ \mu$) epitaxial layers. The OMVPE growth process offers considerable promise as an emerging technique for the growth of high quality III/V semiconductors. However, several questions concerning the fundamentals of the growth mechanism are still unanswered. We have initiated two studies to provide the insight necessary to answer these questions and improve the growth technique.

1) Experiments designed to study the incorporation of carbon in films formed during OMVPE growth have been carefully planned and begun in conjunction with

CHARLES EVANS & ASSOCIATES

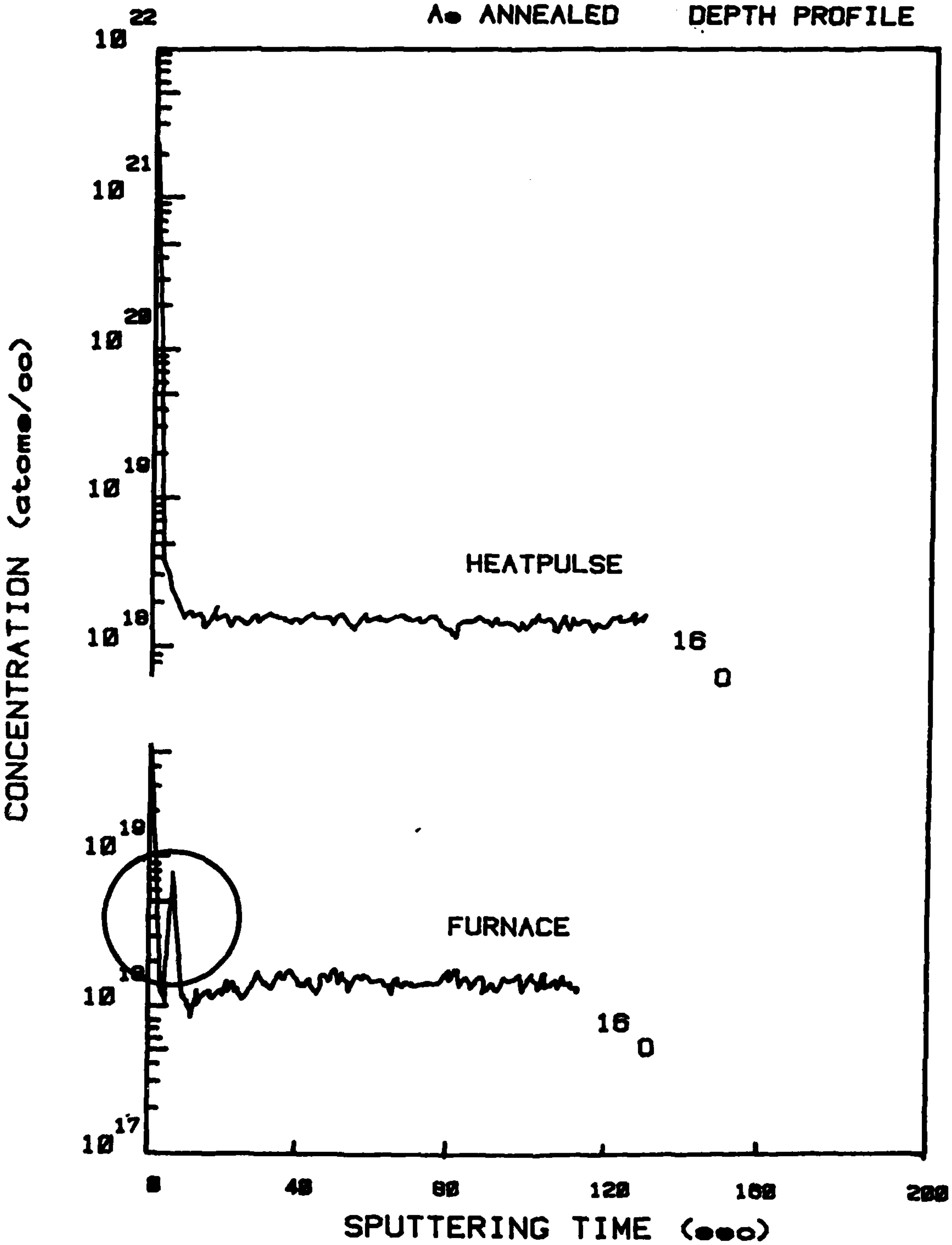


FIGURE 7- SIMS depth profiles of oxygen for $1x10^{15}$ As^{+}/cm^{2} into silicon. Furnace annealed sample shows high oxygen concentration near R_p of implant.

Professor G. Stringfellow of the Department of Electrical Engineering at the University of Utah. Thin films have been grown by OMVPE using methane isotopically enriched in ^{13}C. The goal c this collaboration is directed toward answering the following question regarcing the atomic mechanism involved in the OMVPE growth process:

> "Does the organometallic compound decompose in the gas phase above the growing film and the atomic decomposition products cascade to the surface or does the decomposition occur after adsorption of the molecule onto the surface?"

By using isotopically labeled carbon in the organometallic molecule and performing SIMS depth profiling of both ^{12}C and ^{13}C, it should be possible to answer this very fundamental question.

Unfortunately, because of delays in the early stages of experimentation at Professor Stringfellow's laboratory (principally construction of the epi-reactor and procurement of the necessary isotopically labeled chemicals), we were unable to complete this experiment by the Phase I project deadline. Preliminary results were obtained suggesting one possible mechanism, but the issue is of such a critical nature to the understanding of OMVPE growth that we are going to continue the experiments past June 30 in an attempt to establish a conclusive result. We will have verified the results of this work by the submission date for our Phase II proposal.

2) While attending the 1982 Electronic Materials Conference at Colorado State University, it became evident that OMVPE grown GaAs is subject to the random

incorporation of unintentional donor and acceptor impurities. The exact source of these impurities, however, is not known. Low carrier concentrations have been obtained by varying growth parameters (i.e. growth temperature, III/V ratio, and gas pressure) but the operative donor and acceptor species remain unidentified. The methods for growing high purity OMVPE layers are still very empirical, and often result in high fabrication costs. Identification of the specific residual impurities could result in an improved understanding of their incorporation during the growth process and could eventually provide considerable insight into more efficient film growth procedures.

OMVPE grown GaAs films which show a decrease in N_D-N_A concentrations with an increase in the arsine to trimethyl gallium ratio in the gas phase of the growth process have been obtained from Dr. J. Parsons of Hughes Research Laboratory in Malibu, California. Figure 8 shows the measured carrier concentration as a function of $AsH_3/(CH_3)_3Ga$ for these films. We have initiated a SIMS analysis of these films in an attempt to identify a single impurity or a series of compensating impurities which could produce the correlation between carrier concentration and III/V ratio. However, due to the fact that we only recently became aware of the potential importance of this impurity problem, we do not as yet have the answer. We intend to investigate this area, and hope to provide insight into the issue before preparing our Phase II proposal.

E) <u>Liquid Phase Epitaxy (LPE) and the Use of Other Surface Spectroscopies</u>

In order to demonstrate our ability to expand into other surface sensitive spectroscopies (other than SIMS) in the study of crystal growth techniques,

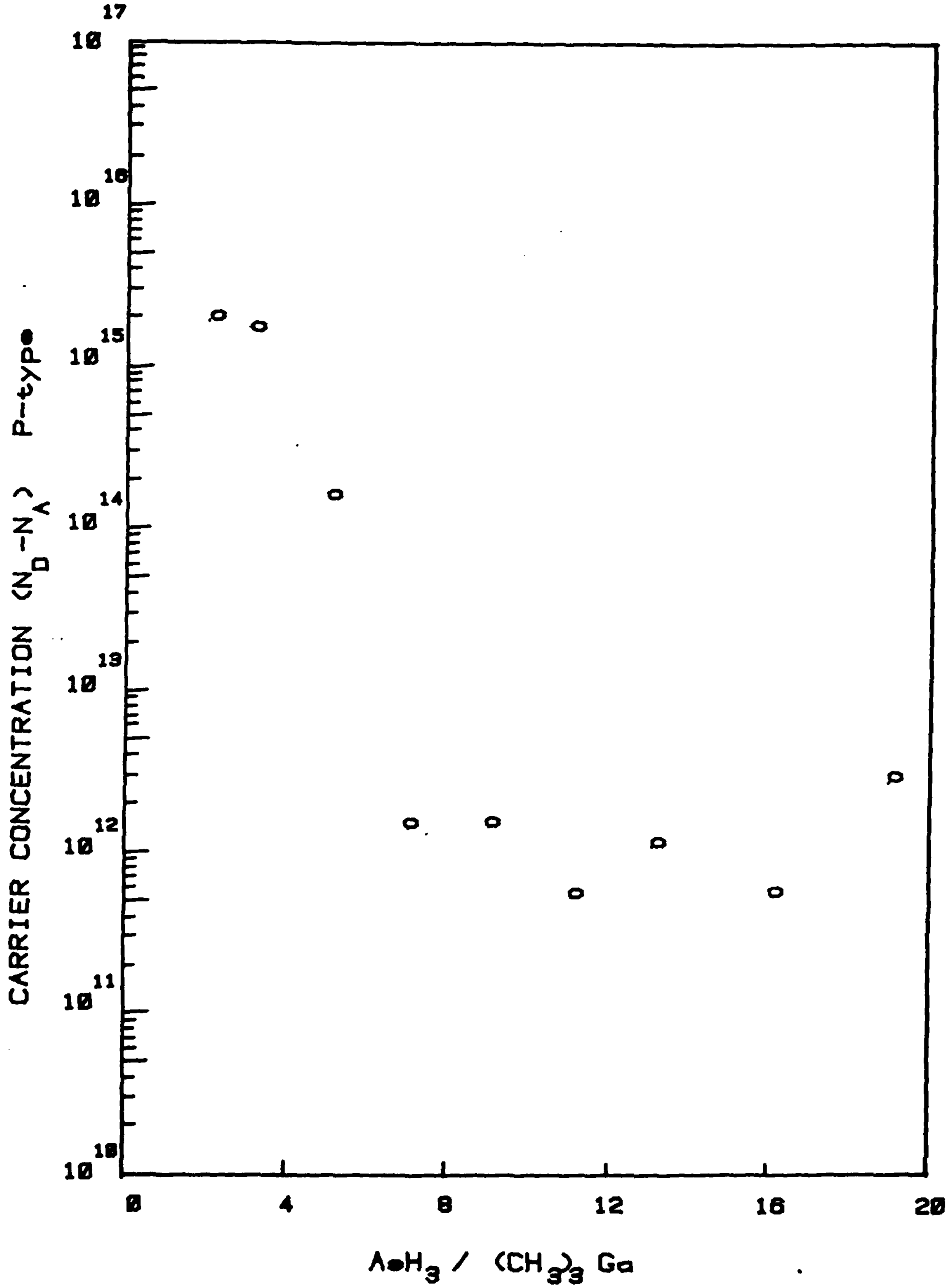


FIGURE 8- Carrier concentration (N_D-N_A) as a function of arsine and trymethyl gallium.

Liquid Phase epitaxial GaAsSb films of varying crystalline quality were analyzed using combined scanning electron microscopy (SEM), Auger electron spectrometry (AES), and energy dispersive X-ray spectrometry (EDS), the JEOL JAMP-10. The LPE films were grown by Professor G. Stringfellow at the University of Utah. The results of this study indicated that the initial LPE films were multiphased. The grown layer is composed of regions of the desired GaAsSb but also contained islands of GaSb. Secondary electron micrographs showed evidence of polycrystallinity, defects and contamination in the substrate material. A good correlation was established between the quality of the epitaxial layer and the quality of the substrate. Examination of these results and the growth processes lead us to conclude that in areas where there were large surface defects or contamination no GaAsSb epi-growth took place. Thus, holes existed in the epitaxial layer which were then filled with the GaSb melt producing the two phases observed in the grown layers. Both surface morphology and phase stoichiometry could be determined using these surface sensitive analytical techniques.

The combined SEM/AES/EDS technique provides the capability of detailed characterization of major and minor constituents while SIMS permits dopant and trace level impurity analysis required for the complete characterization of the composition of films grown by any of the crystal growth techniques discussed in this report.

IV. CONCLUSION

The results of this Phase I research effort have demonstrated the importance of combining carefully planned crystal growth experiments with surface sensitive spectroscopies in order to elucidate the fundamentals of single crystal growth techniques. The key to the success of this research program has been the following:

1) the recognition that crystal growth involves three dimensional motion of atoms unobservable during the growth process.

2) strategic planning of experiments which label this motion for subsequent optimized analysis.

3) careful analysis and data interpretation so as to elucidate any particular crystal growth mechanism/phenomenon in the context of the experimental technique.

DATE
FILMED
-8